

Prediction of new crystal structure phases in metal borides: a lithium monoboride analog to MgB_2 .

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(Dated: February 4, 2008)

Modern compound prediction methods can efficiently screen large numbers of crystal structure phases and direct the experimental search for new materials. One of the most challenging problems in alloy theory is the identification of stable phases with a never seen prototype; such predictions do not always follow rational strategies. While performing *ab initio* data mining of intermetallic compounds we made an unexpected discovery: even in such a well-studied class of systems as metal borides there are previously unknown layered phases comparable in energy to the existing ones. With *ab initio* calculations we show that the new metal-sandwich (MS) lithium monoboride phases are marginally stable under ambient conditions but become favored over the known stoichiometric compounds under moderate pressures. The MS lithium monoboride exhibits electronic features similar to those in magnesium diboride and is expected to be a good superconductor.

Development of theoretical methods able to guide the experimental search for new materials with desired properties is a fast-growing field of research in materials science[1, 2, 3, 4, 5, 6, 7, 8]. A particular effort has been put into the coupling of *ab initio* electronic structure methods with efficient data-mining algorithms to determine and utilize correlations in binding mechanisms in a chosen set of structures[4, 5, 6, 7]. However, even with the most advanced optimization algorithms one has to restrict the search space to a given structure[4], lattice type[5], or prototype library[6, 7]. Moreover, in some approaches structures are kept symmetry-constrained or not relaxed at all. Considering the rich nature of bonding in solids, such limitations can lead to overlooking the most stable phases. This makes identification of new prototypes a vital step towards a more complete description of alloys.

Expanding the library of *ab initio* energies of binary alloys described in Ref. [6] we observed that one of the phases in the Mg-B system, A_2B_2 fcc-(111) (or V2 [9]), unexpectedly underwent significant structural relaxation and became comparable in energy to the mixture of two coexisting stable phases, MgB_2 and hcp-Mg. Upon examination of the relaxation process we found that there is a continuous symmetry-conserving path from V2 (Fig. 1c) to a new metal-sandwich (MS) structure MS1 (Fig. 1b)[10]. The latter has four atoms per unit cell with hexagonal layers of boron separated by two triangular layers of metal; it bears strong resemblance to the AlB_2 prototype (Fig. 1a) having a similar sp^2 boron-boron bonding. The extra metal layer is inserted in a close-packed fashion with Mg-Mg bond length close to that in the pure hcp structure, which may account for the near-stability (by a few meV/atom) of the magnesium monoboride. To the best of our knowledge, this structure has not been considered before for any binary alloy. We have constructed a series of related MS structures with different stacking sequences of metal and boron layers (such as MS2 in Fig. 1d[11]), which is a generalization of the

MS1 prototype.

The identification of the MS structures has prompted us to re-visit metal borides, which have lately been a focal point in the search for new superconducting materials, following the discovery of superconductivity in MgB_2 with a surprisingly high transition temperature of 39 K[12]. The high T_c in MgB_2 was explained as due to a very strong electron-phonon coupling of the E_{2g} mode to the hole-like $p\sigma$ -states of boron[13]. These states are also crucial for structural stability of metal diborides and their availability in these compounds implies weak binding[14]. This feature makes the effectively electron-doped (because of the extra metal layer) MS1 structure a particularly good candidate to be a stable configuration for low-valent metal borides. We have investigated a large set of alkali, alkaline and transition metal borides

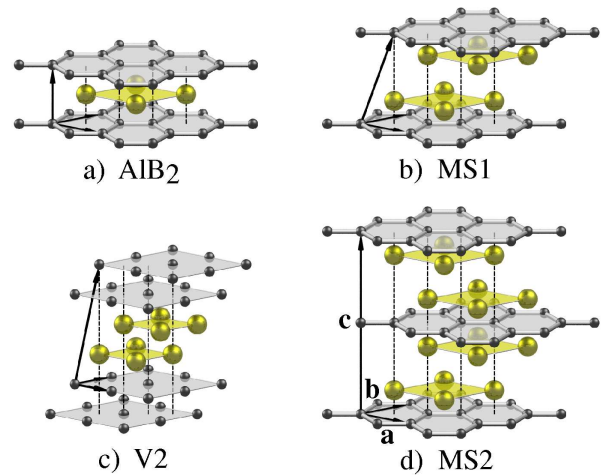


FIG. 1: (color online). Known (AlB_2 , V2) and proposed metal-sandwich (MS1, MS2) prototypes. The hexagonal layers of boron (grey) are separated by triangular layers of metal (yellow, only four atoms per layer are shown).

with *ab initio* calculations and found that MS1 and MS2 phases in one system, Li-B, are indeed stable enough to compete against known phases.

Present *ab initio* simulations have been performed with VASP [15, 16]; we use projector augmented waves (PAW) [17] and exchange-correlation functionals as parametrized by Perdew, Burke, and Ernzerhof (PBE)[18] for the Generalized Gradient Approximation (GGA). For comparison purposes we carry out tests in the Local Density Approximation (LDA)[19], and with ultrasoft (US) pseudopotentials[20]. We also employ an LAPW code WIEN2K [21] to plot characters of electronic bands and partial density of states (PDOS). All structures were fully relaxed. Numerical convergence to within about 2 meV/atom is insured by high energy cut-off (398 eV) and dense k-meshes[22].

Despite the potentially important application to batteries, the Li-B system is not fully explored and the question of the most stable monoboride phase remains open[24, 25, 26, 27]. Successful experimental attempts to synthesize lithium monoboride under ambient pressure date back to the 1970s[28, 29]. However, the structure of α -LiB, shown in Fig. 2a, has been identified only recently[25, 27, 30]. A theoretical study suggests that lithium atoms in the lithium monoboride could be subject to low-energy motion along the linear boron chains, as α -LiB and a related β -LiB phase (NiAs prototype, see Fig. 2b) were found to be nearly degenerate[26].

We compare our MS lithium monoboride to the known stoichiometric phases directly, using the experimentally observed α -LiB as a reference point. The following results may contain relatively big systematic errors (i.e. due to approximations in the exchange-correlation functional and in the treatment of the charge density), since we consider structures with different types of boron-boron bonding. We find that the MS1-LiB phase is 3 meV/atom lower in energy than α -LiB and about 7 meV/atom higher than β -LiB[31]. The α -LiB and β -LiB phases differ by a noticeable 10 meV/atom, a surprising result considering that our fully-relaxed cell parameters (α -LiB: $a = 4.026$ Å, $c = 3.112$ Å and β -LiB: $a = 4.010$ Å, $c = 3.119$ Å) closely match the reported LDA values[26]. We check the sensitivity of these results to the approximation used by carrying out two more tests with WIEN2K (LAPW, in the GGA-PBE) and VASP (PAW-LDA).

The relaxed cell parameters in the LAPW-GGA calculations are nearly the same as in the PAW-GGA[10, 11]. In this approach MS1-LiB is a little lower in energy (13 meV/atom below α -LiB) and the most stable of the three[32]. The PAW-LDA gives a much lower relative energy for MS1-LiB (42 meV/atom below α -LiB). A big discrepancy in the description of relative energies with the two approximations has also been seen in carbon systems with different types of bonding[33]; the GGA is expected to be more accurate. In all the tests above α -LiB and

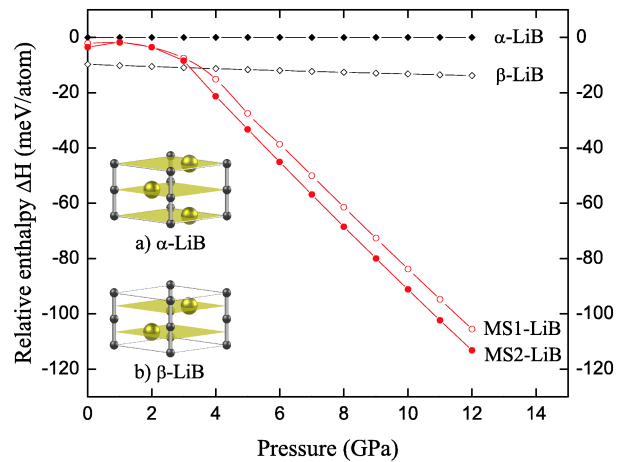


FIG. 2: (color online). Calculated relative enthalpy, $\Delta H(P) \equiv H(P) - H_{\alpha\text{-LiB}}(P)$, as a function of pressure for lithium monoboride phases. The points are connected with splines. The larger yellow spheres are lithium atoms and the smaller black spheres connected with sticks are boron atoms.

β -LiB remain 10 meV/atom apart. The independence of this result on the calculation approach can be explained by the similarities of the two structures, a trend also observed in other systems[34].

We conclude that within the accuracy of these calculations the MS1-LiB phase is comparable in energy to the known phases. Synthesis conditions could therefore be the deciding factor for which compound forms in the Li-B system at 50% concentration. We next evaluate the effect of hydrostatic pressure on the relative stability of the lithium monoboride phases. The three phases have very close volumes per atom at zero pressure. However, the α -LiB and β -LiB with linear boron chains are much harder than the sp^2 -bound MS1-LiB: the respective volumes at $P = 12$ GPa are about 85%, 85%, and 69% of the zero-pressure values (interestingly, the intralayer bonds in MS1-LiB undergo non-monotonous expansion with pressure, stretching by about 2% at 5 GPa). The big compressibility of the MS1-LiB is an expected feature for a layered structure with a weak interlayer binding: at $P = 12$ GPa the c-axis shrinks down to 68% of its zero-pressure value, primarily due to the decrease in the Li-Li interplanar distance. The weakening of the metallic binding in the lithium bilayer is apparently caused by the significant charge transfer from lithium to the boron layer. The extreme softness of MS1-LiB suggests use of high pressures for synthesis of this phase. We plot the calculated enthalpies of the considered lithium monoboride phases with respect to α -LiB versus external pressure in Fig. 2. The plot shows that even if the MS-LiB are not the most stable phase at ambient pressure, they are quickly driven below the known phases and become favored by over 90 meV/atom at $P = 12$ GPa[35]. Note, that the hydrostatic pressure removes the degenerate

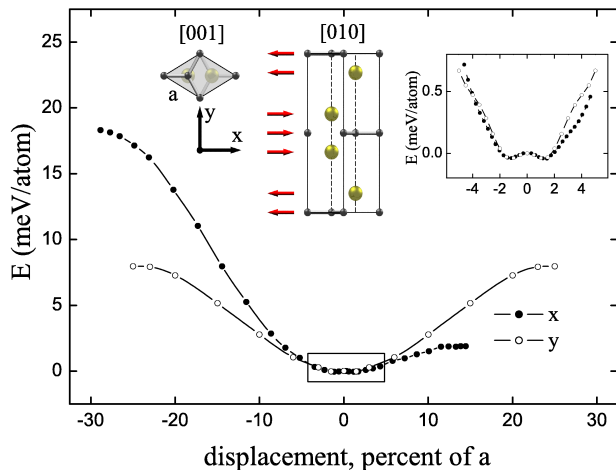


FIG. 3: (color online). Slices of the potential energy surface in MS2-LiB along the eigenvectors of the softest phonon modes at Γ . The modes represent the interlayer sliding in the x (see the [010] view) and y directions of undistorted boron layers rigidly locked with the adjacent lithium layers. The inset demonstrates two shallow minima at small displacements. *Ab initio* data points are connected with splines.

eracy of the MS1-LiB and MS2-LiB, different only by a long-period stacking shift: the pressure favors MS2-LiB, in which the flatness of the boron layers is enforced by symmetry. Use of appropriate substrates could also promote growth of the new layered structures.

An important question is how to detect the new phases if they indeed form. Because the MS1 and MS2 are nearly degenerate at low pressures, the resulting structure at 50% concentration in Li-B could be a random mixture of the two and would be hard to detect with standard x-ray methods. Fortunately, the two phases have similar interlayer distances for boron and one would expect to see an x-ray peak (at $\lambda = 1.5418 \text{ \AA}$, zero pressure) in the range from $2\theta = 16.1^\circ$ for MS2 to $2\theta = 16.6^\circ$ for MS1. None of the observed peaks in the samples prepared at ambient pressure[25] match these calculated values. Experimental effort to synthesize lithium monoboride at high pressures is highly desired.

Ab initio studies have shown that existence of energetically favorable phases could be barred by dynamical instabilities[36]. We have investigated phonon modes at Γ -point with a force-constant matrix diagonalization method, implemented in VASP, using the MS2 structure with a convenient rhombohedral unit cell. MS2-LiB has two weakly interacting boron layers per unit cell which leads to an effective double-degeneracy of the known phonon modes at Γ in the AlB_2 -type compounds. Three of the remaining six optical modes, which involve sliding of undistorted layers, are rather soft. The soft modes are defined by the weakened interlayer Li-Li interaction and the perfectly stacked structure may actually be prone to small interlayer shifts, as there are two shallow minima

at about 2% displacements of the in-plane lattice vector a (see Fig. 3). We crudely estimate the frequency of the soft modes at Γ by using all points up to 5% displacements and obtain $\omega_{x,y} = 55 \text{ cm}^{-1}$ and $\omega_z = 86 \text{ cm}^{-1}$. The modes at the A point are slightly softer ($\omega_{x,y} = 37 \text{ cm}^{-1}$ and $\omega_z = 59 \text{ cm}^{-1}$) but they remain real (interestingly, the frequencies are comparable to those in another layered structure, graphite[37]). The interlayer sliding phonon modes along the Γ -A direction are expected to be the softest optical phonon modes in the whole Brillouin zone: any finite $k_{x,y}$ would result in distortions of the rigid boron or lithium layers and a consequent phonon hardening. These considerations indicate that the MS2-LiB phase is dynamically stable. Hydrostatic pressure is again found to be a stabilizing factor: already at $P=2 \text{ GPa}$ the small distortions are suppressed and the frequencies of the softest x-y phonon modes are nearly doubled. Calculation of phonon modes for the full Brillouin zone is a subject of future study. With all the phonon branches calculated one can also estimate the vibrational entropy contribution to the Gibbs free energy to complete the analysis of the thermodynamic stability of MS-LiB.

The investigation of the phonon modes reveals that the actual stable unit of the MS-LiB phases is a hexagonal boron layer coated with two lithium layers on each side and can be related to graphene. Indeed, according to our estimates the cohesion per area between these B_2Li_2 sheets and their curvature energy are comparable to those for a carbon layer[34]. One could speculate that if MS-LiB was exfoliated into such sheets, they might form carbon-like tubular or nanoporous structures. It would be interesting to see whether stable MS compounds could be obtained in other intermetallics based, for instance, on beryllium. Going beyond binaries also seems a promising direction to find more stable compounds: additional metal sites give more flexibility to experiment with different ternary alloys.

Finally, we give a brief discussion of the electronic properties of the MS phases focusing primarily on the p -states in boron, important for superconductivity in metal diborides. Our LAPW calculations [21, 38] show that the boron $p\sigma$ band along Γ -A in MS2-LiB has practically no dispersion (Fig 3), an expected feature caused by the large separation between boron layers. Compared to a hypothetical $\text{AlB}_2\text{-LiB}_2$ phase the Γ -A band downshifts by 0.6 eV and the $p\sigma$ PDOS at Fermi level drops by 25% to $N_{p_{xy}}^B(0) = 0.046 \text{ states/(eV}\cdot\text{spin)}$ per boron atom, which indicates higher filling of these bonding boron states. Note, that bonding $p\pi$ states also become occupied (E_F is located exactly in the middle of the $p\pi$ pseudo-gap). The combination of these effects explains the dramatic stabilization of the lithium monoboride. Remarkably, the $p\sigma$ PDOS in MS2-LiB stays about 12% higher than that in MgB_2 .

We find the frequency of the anharmonic E_{2g} mode at Γ -point (649 cm^{-1}) in MS2-LiB to be quite close to

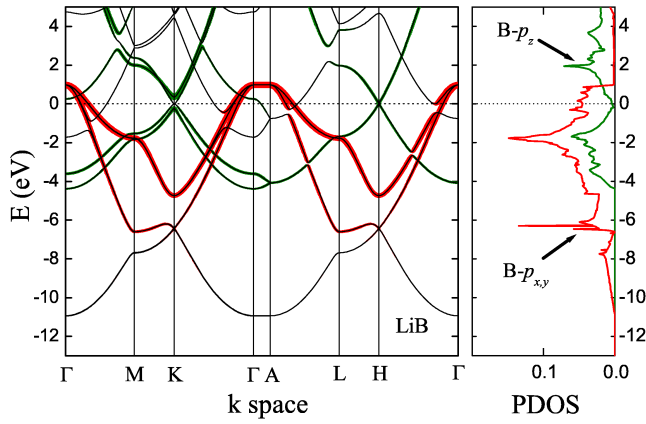


FIG. 4: (color online). Band structure and partial density of states (PDOS) in MS2-LiB, calculated in LAPW[21, 38]. PDOS units are states/(eV·spin) per boron atom. The thickness of band structure lines is proportional to boron $p_{x,y}$ (red) and p_z (green) characters.

that (624 cm^{-1}) in MgB_2 [39], which can be related in part to the almost perfect match of the covalent boron-boron bond lengths[11]. The similarities of the boron layer properties in these borides appear to extend to the electron-phonon coupling as well: following procedure in Ref. [42], we estimate the deformation potential \mathcal{D} for the E_{2g} mode to be 13 eV/\AA in both phases. Unlike the two-band superconductor MgB_2 , MS2-LiB has negligible contribution from the boron $p\pi$ states at E_F . These simple arguments suggest that the superconducting T_c in the MS2-LiB would be at least comparable to that in MgB_2 .

In conclusion, this work demonstrates that our knowledge of binary alloys is still incomplete and the identification of yet unknown phases may require new prediction strategies. The rather accidental finding of the MS phases should be credited to the exhaustive consideration of all candidates used in our data-mining approach and the careful structural relaxation in the calculation of their ground states. The MS structures are shown to be particularly suitable for the Li-B system: lithium monoborides are marginally stable under ambient conditions but become favored over the known stoichiometric compounds under pressure. The effectively electron-doped MS-LiB phases retain a significant PDOS from the $p\sigma$ -boron states at E_F and could be the long-sought non-magnesium-based high T_c metal boride. Moreover, relative to MgB_2 the MS-LiB phases are demonstrated to be hole-doped; if synthesized, they would provide valuable information on how the hole-doping affects the T_c in stoichiometric metal borides and whether MgB_2 really has the highest possible T_c in its class[43, 44, 45, 46].

We thank F.H. Cocks, V. Crespi, P. Lammert, R. Margine, and J. Sofo for valuable discussions.

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- [11] MS2: 8 atoms, space group $P6_3/mmc$ (#194). $a = b$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$, Wyckoff positions: M (4f) (1/3,2/3,1/4- z_M /4), B1 (2b) (0,0,1/4), B2 (2d) (1/3,2/3,3/4). $a=3.057 \text{ \AA}$, $c=11.04 \text{ \AA}$, $z_M=0.496$.
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- the MS1-LiB is 12 meV/atom below α -LiB.
- [32] We use $R_{MT}^B = 1.35$ a.u., $R_{MT}^{Li} = 1.8$ a.u., $R_{MT} \cdot K_{max} = 8.0$, $l_{max} = 10$ and require the charge convergence to within 10^{-4} . Since boron-boron bond lengths in the linear chains and in the hexagonal layers are quite different (by about 13%) we also check the dependence of the results on the muffin-tin radii used. Increasing R_{MT}^B to 1.45 a.u. in α -LiB, R_{MT}^B to 1.6 a.u. in MS1-LiB and R_{MT}^{Li} to 2.0 a.u. in both (the MT spheres do not overlap) changes the relative energies by less than 2 meV/atom. LAPW and APW+lo[21] basis sets produce nearly identical results.
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